Raman spectroscopy calibration/analysis/errors – large scale containers

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Topics

- Brief overview of the measurement method.
- Measurement results to date on large cans.
- Methods used to convert raw data to partial pressures.
- Detection thresholds and how they are defined and determined.

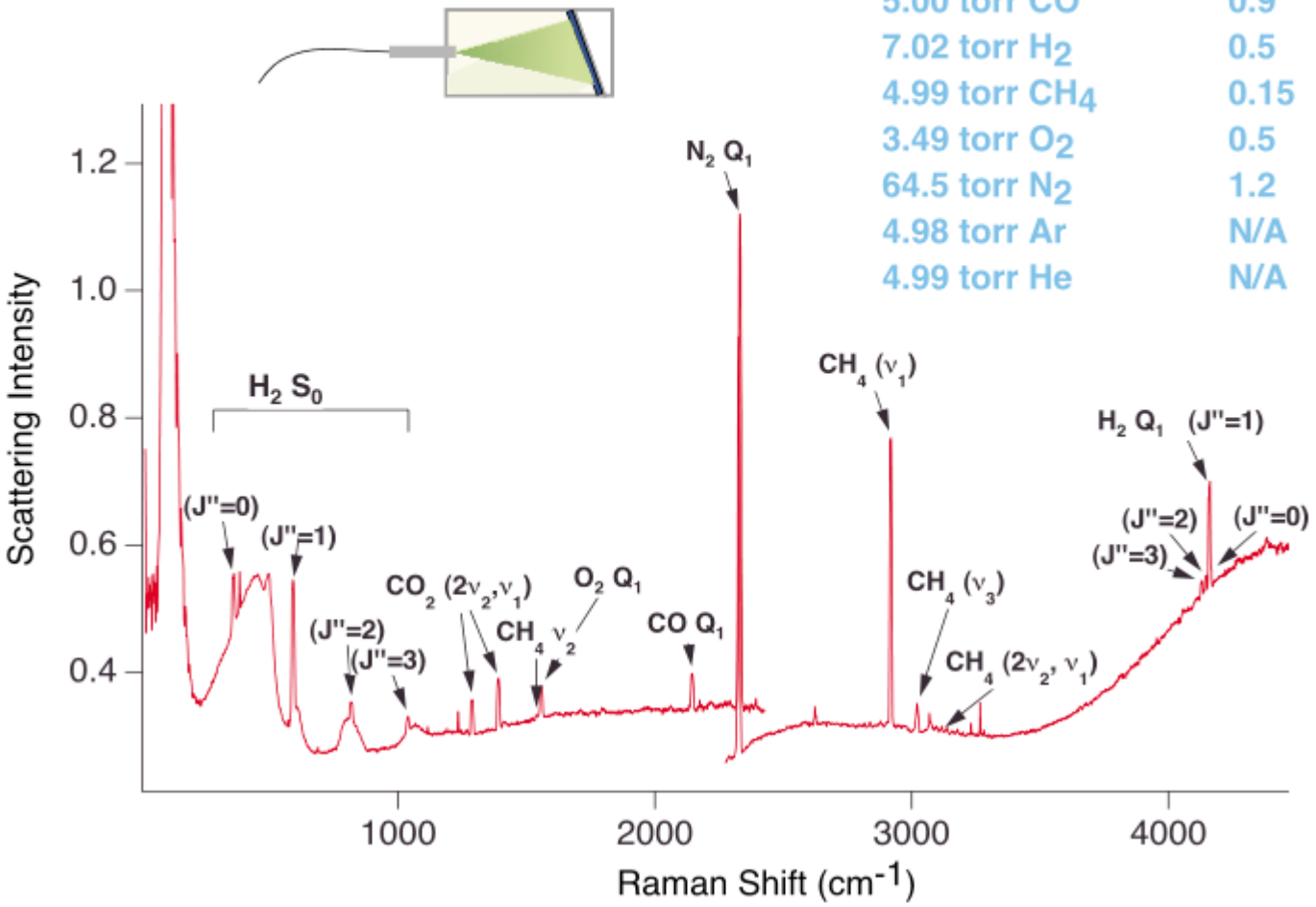
Overview of Raman application

- Raman spectroscopy scatters light off of a sample and measures the scattered intensity as a function of wavelength.
- Each molecule scatters at characteristic wavelengths which are well known, allowing straightforward identification.
- Intensity is proportional to concentration.
- Fiber optics deliver and collect light.

Calibration gas mixture in Raman sample chamber

10 min. at 0.5 watts

Composition	Detection Threshold (torr)
5.02 torr CO_2	0.5
5.00 torr CO	0.9
7.02 torr H_2	0.5
4.99 torr CH_4	0.15
3.49 torr O_2	0.5
64.5 torr N_2	1.2
4.98 torr Ar	N/A
4.99 torr He	N/A



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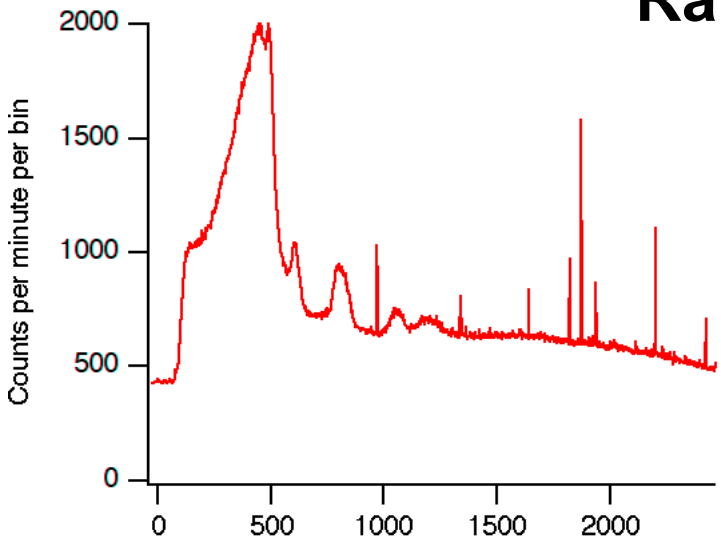
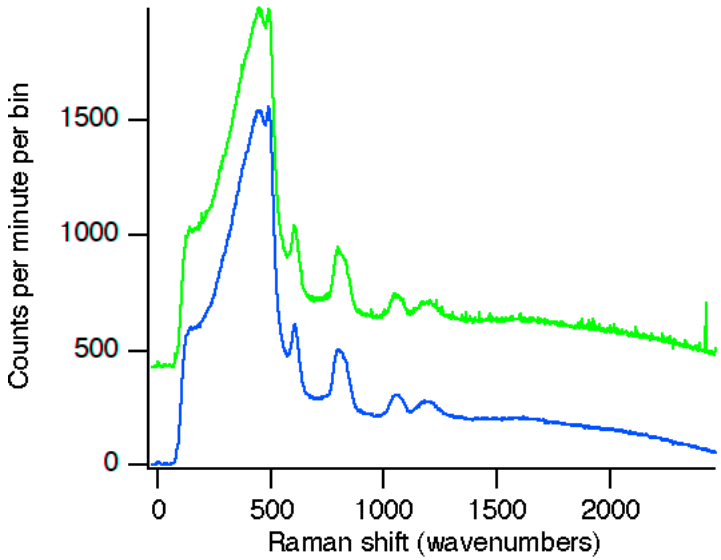
Methods of data treatment

- Raw data contain artifacts due to ionizing radiation hitting the detector (cosmic rays and local background). These are rare events that are removed by threshold filtering.
- Noise on inevitable background signal is reduced by signal averaging. It is the limiting factor in determining sensitivity.
- Detection thresholds are defined as the gas pressure that would produce a peak 5 times the amplitude of the background signal standard deviation.

Raman data treatment



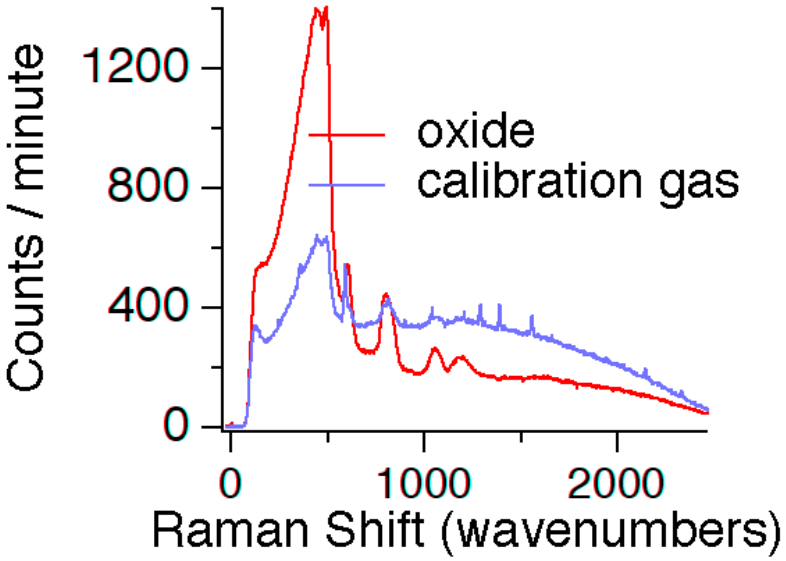
Raw spectrum, 1 minute



Average of 10, outliers discarded

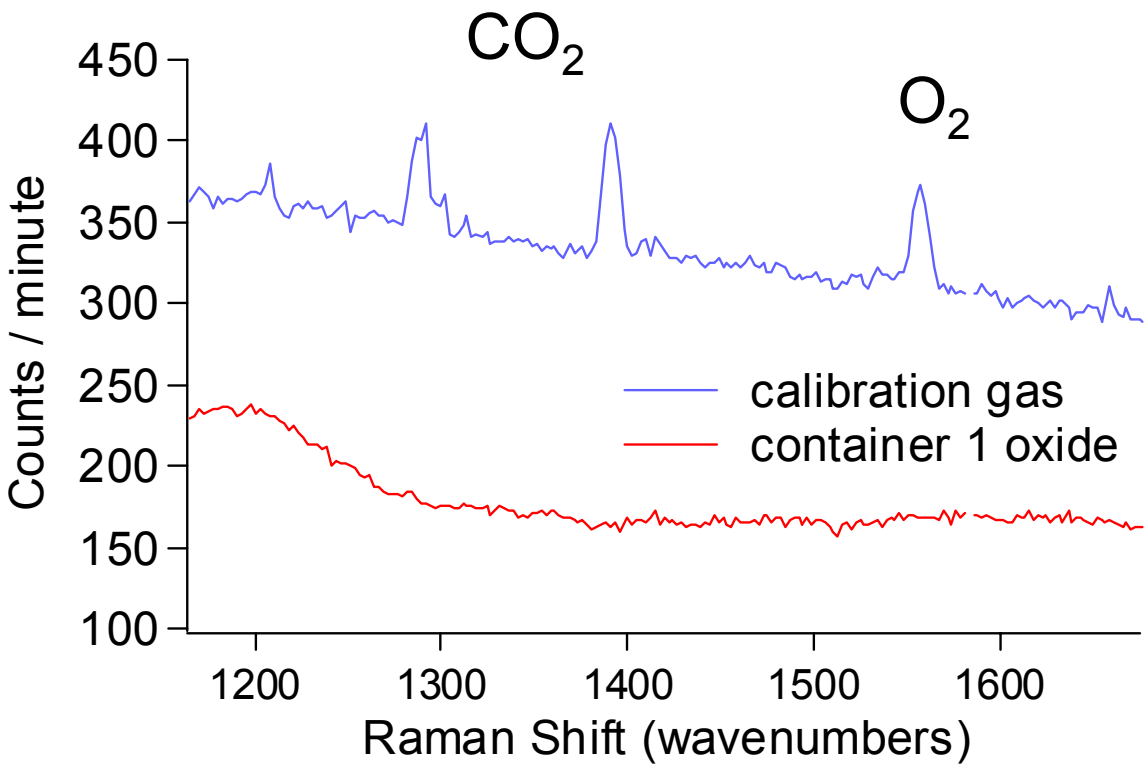
Detector background subtracted

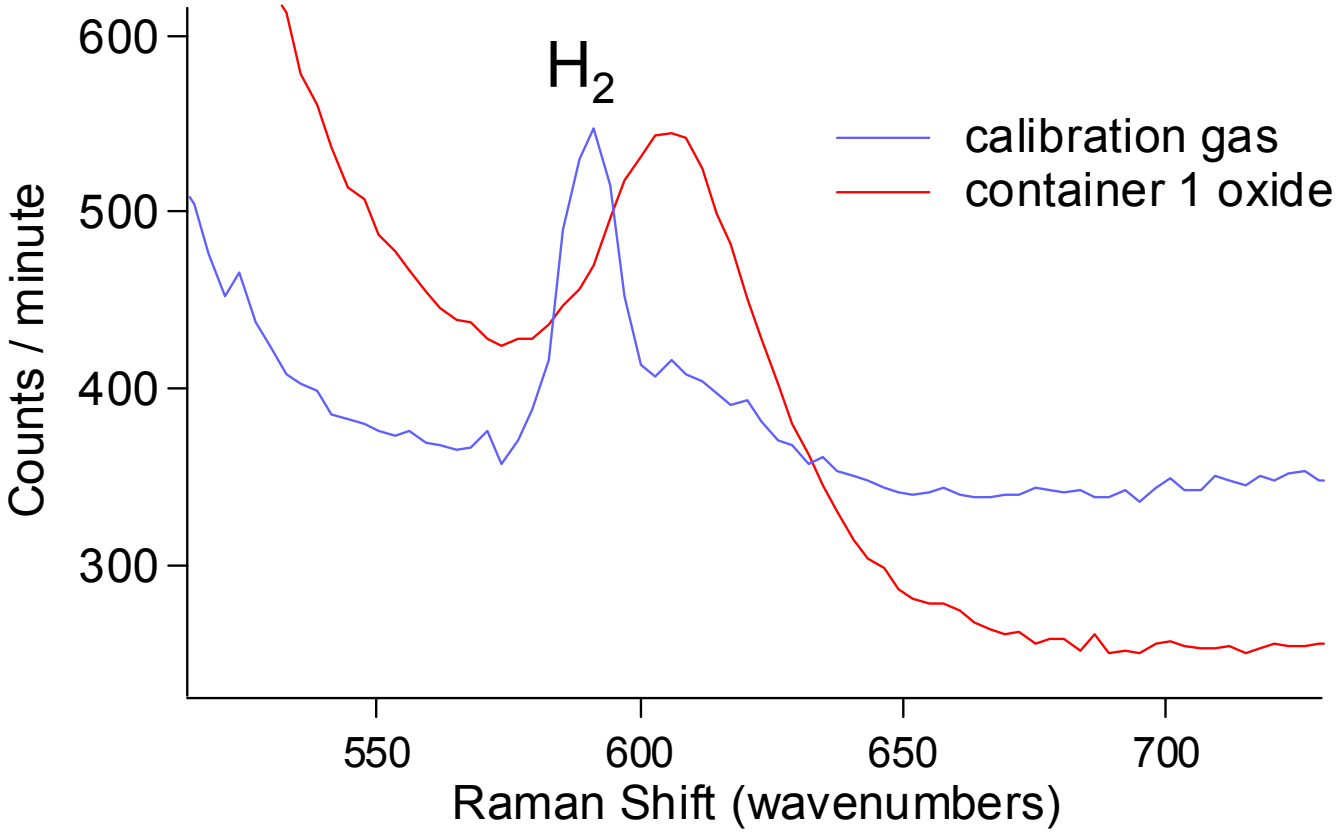
Typical Raman data



- Calibration gas included H_2, O_2, N_2, CO and CO_2.
- Gas signals do not vary appreciably between probes.

Container 1 shows no Raman-detectable gases after > 9 months.




H2
calibration gas
container 1 oxide
Counts / minute
600
500
400
300
550
600
650
700
Raman Shift (wavenumbers)

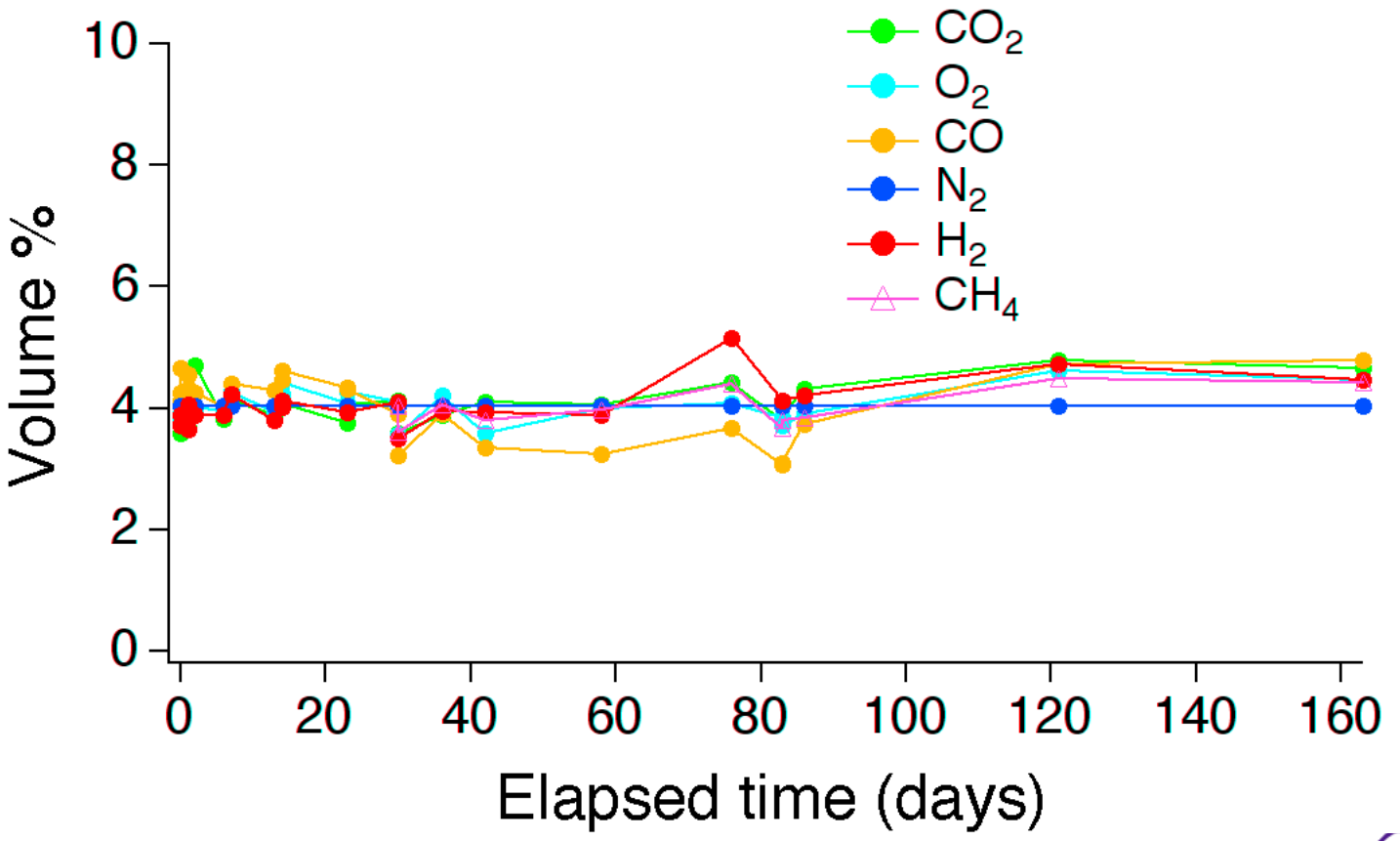
Raman Detection Thresholds for Container 1

Gas pressure that would produce a peak 5 times the amplitude of the background signal standard deviation in 10 minutes.

	Torr	psi	std. atm.
H_2	3	0.06	0.4 %
O_2	4	0.08	0.5 %
CO_2	4	0.08	0.5 %
N_2O	4	0.08	0.5 %
N_2	10	0.08	1.3 %

Calibration Gas Mixture in Empty Can

- Normalized to N_2 known value of 4.03%.
- Standard deviations of 5 to 8 %.



Application to Containers

- Raman is in-situ measurement, consuming no gas.
- Measurement frequency not limited by need to conserve sample.
- Initial measurments taken several per day.
- Measurement rate tapering to once per month after 3 months.

Summary

- Pure oxide in Container 1: no Raman signals from detectable gases (essentially everything but noble gases).
- Detection thresholds for 10 minute acquisitions are conservatively estimated at 3 torr for H_2, 4 torr for O_2, CO_2 and N_2O, and 10 torr for N_2.